Synthesis and Characterization of Bis-benzyl and Bis-allyl Complexes of Titanium(III) and Vanadium(III); Catalytic Isomerization of Alkenes with CpV(η3-C3H5)2

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SYNTHESIS AND CHARACTERIZATION OF BIS-BENZYL AND BIS-ALLYL COMPLEXES OF TITANIUM(III) AND VANADIUM(III); CATALYTIC ISOMERIZATION OF ALKENES WITH $CpV(\eta^3\text{-}C_3H_5)_2$

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Summary

Reactions of $CpTiCl_2$ ($Cp = \eta^5\text{-}C_5H_5$) with RMgX (X = Cl, Br) yield the complexes $CpTiR_2$ ($R = CH_2Ph$, $\eta^3\text{-}C_3H_5$). The complex $Cp^★Ti(\eta^3\text{-}C_3H_5)_2$ ($Cp^★ = \eta^5\text{-}C_5Me_5$) was prepared analogously from $Cp^★TiCl_2(THF)$. $CpVCl_2(PEt_3)_2$ and $Cp´VCl_2(PEt_3)_2$ ($Cp´ = \eta^5\text{-}C_5H_4Me$) were used for the preparation of $CpV(CH_2Ph)_2$, $CpV(\eta^3\text{-}C_3H_5)_2$, $CpV(\eta^3\text{-}1\text{-}MeC_3H_4)_2$ and $Cp´V(\eta^3\text{-}C_3H_5)_2$, respectively. The corresponding $Cp^★V$ derivatives could not be obtained. The reaction of $CpCrCl_2(thf)$ with C_3H_5MgCl gives a dimeric complex $[CpCr(C_3H_5)]_2$, probably via intermediate formation of $CpCr(C_3H_5)_2$. CpV-bis-allyl complexes are active in the catalytic isomerization of alkenes; a 1,3-hydride shift via a π-allylmetal hydride species is proposed. In contrast no activity in isomerization was observed for $CpTi(C_3H_5)_2$ and $Cp^★Ti(C_3H_5)_2$.

Introduction

As part of our study of monocyclopentadienyl complexes of early transition 3*d* metals we embarked upon a study aimed at preparing mono-CpM-alkyl, -aryl and --allyl species and to exploring their chemical reactivity.

Convenient starting compounds of the type $CpMX_2L_n$ (M = Ti, Cr; X = Cl, Br; L = two electron donor ligand; n = 0, 1, 2) are well known [1]. We recently reported the preparation of the first vanadium derivatives of this type, viz. $CpVX_2(PR_3)_2$ (X = Cl, Br; R = Me, Et) [2]. The replacement of halide ligands in $CpMX_2L_n$ by reaction with the appropriate Grignard and lithium reagents was examined (eq. 1).

$$CpMX_2L_n + 2\ RM´ \rightarrow CpMR_2L_m + (n - m)L + 2\ M´X \quad (1)$$

(M = Ti, V, Cr; X = Cl, Br; M´ = Li, MgX; n = 0, 1, 2; $m = \leq n$)

Some such work has already been carried out with titanium compounds. Green

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and Lucas [3] tried to prepare $CpTiR_2$ (R = Me, CH_2SiMe_3) starting from $CpTiCl_2$ with RMgBr or RLi in ether at room temperature. They isolated only the tetravalent Ti species $CpTiR_3$ in low yield. Apparently disproportionation occurred into an unknown titanium(II) species and the titanium(IV) species. Their attempts to prevent disproportionation by using $CpTiCl_2L_2$ (L = PMe_2Ph, $PMePh_2$) or $CpTiCl_2$(L-L) (L-L = dmpe, dppe) as starting compounds were also unsuccessful and no $CpTiR_2$ (R = Et, n-Bu, allyl, phenyl) or the corresponding phosphine adducts were isolated. The formation of the butadiene-methallyl derivative $CpTi(\eta^4\text{-}C_4H_6)(\eta^3\text{-}1\text{-}MeC_3H_4)$ in the reaction of $CpTiCl_2$ with the appropriate allylic Grignard as observed by Zwijnenburg et al. [4] seems to be in agreement with Green's results. Butene elimination from $CpTi(1\text{-}MeC_3H_4)_3$, formed by disproportionation, could account for the formation of the observed butadiene complex. The only $CpTiR_2$ complex previously reported in the literature is the bis-benzyl derivative $CpTi(CH_2Ph)_2$ [5]; this was prepared from Cp_2TiCl_2 by reaction with benzyllithium. Built-in two-electron donor atoms in the ligands R also can enhance the stability of $CpTiR_2$; thus, the chelating ligands in $CpTi(C_6H_4\text{-}o\text{-}CH_2NMe_2)_2$ provide considerable stabilization [6], and thus the complex can be regarded as a complex of the type $CpMR_2L_2$.

No $CpVR_2$ complexes have been reported. Because of the known results for titanium, our first aim was to explore the unknown vanadium chemistry.

Results and discussion

Exploratory studies

Replacement of the halide ligands of $CpVX_2(PEt_3)_2$ was attempted using a stoichiometric amount of various alkyl- and aryl-Grignard reagents RMgX (X = Cl, Br). It was hoped that the paramagnetic complexes of the type $CpVR_2(PEt_3)_n$ (n = 0, 1, 2) would be formed, and be sufficiently stable to be isolated. We tried the reactions for R = Me, n-Bu, neo-Pe and phenyl; in all cases a fast reaction took place even at -80°C, and dark solutions were formed, but no tractable vanadium complexes were formed.

Partly liberation of PEt_3 was shown by GLC. Attempts to obtain stable metallocyclic species by reaction with 1,4-Li_2-1,2,3,4-Ph_4C_4 (butadiene) or 1,4-$M_2C_4H_8$ (M = Li, MgBr) were also unsuccessful. The formation of ethene in the 1,4-$M_2C_4H_8$ reactions suggests thermal decomposition of an initially formed vanadacyclopentane complex. It is possible that the *trans* arrangement of the halides hamper the formation of a more stable metallocyclic species. A complex with the halide ligands in a *cis* disposition might be more useful in preparing this species, but attempts to prepare the *cis* starting compounds $CpVX_2$(L-L) (L-L is for instance dmpe, dppe) have not yet succeeded [2].

Bis-benzyl compounds $CpM(CH_2Ph)_2$

More straightforward results were obtained with benzylMgBr. The existence of $CpTi(CH_2Ph)_2$ was previously noted by Razavaev et al. [5]. We made it by a different method, viz. by treating $CpTiCl_2$ with two equivalents of benzylmagnesium bromide in ether. The analogous vanadium complex $CpV(CH_2Ph)_2$ is also formed in reaction of $CpVCl_2(PEt_3)_2$ with benzylmagnesium bromide. It was obtained as a red oil, unstable at room temperature, but it can be kept at -20°C for weeks. In

spite of several washings with pentane we were not able to obtain the compound completely free of PEt_3, the IR spectrum still showing coordinated PEt_3. The presence of two benzyl ligands per vanadium was established with an HCl/ether reaction. The analogous reaction with $CpVCl_2(PMe_3)_2$ yielded a solid and the elemental analysis and IR spectroscopy indicate that this is $CpV(CH_2Ph)_2PMe_3$. Apparently PMe_3 is more strongly coordinated than PEt_3, and neither washing with pentane nor pumping vacuum can remove the phosphine ligand.

The IR spectra of $CpTi(CH_2Ph)_2$ and $CpV(CH_2Ph)_2$ are virtually identical, and therefore the complexes are probably isostructural. The benzyl absorptions in the two ranges of interest, viz. aryl-ν(CC) range and aryl-δ in plane (CH) range, correspond to absorptions found in well established η^1-benzyl complexes [7]. In particular the strong absorption at 1590 for Ti and at 1588 cm^{-1} for the V complex is characteristic for η^1-benzyl. In known η^3-benzyl complexes this absorption is weak or even absent [7].

Bis-allyl compounds $CpM(C_3H_5)_2$

The results with benzyl ligands prompted us to use small allylic ligands. Their steric bulk is less than that of benzyl ligands and therefore a stable η^3-coordination mode might be attained. We first discuss our results for titanium. Green and Lucas [3] could not obtain $CpTi(C_3H_5)_2$ from their $CpTiCl_2L_2$ system. We tried, starting from $CpTiCl_2$ suspended in ether, and were able to isolate the thermally stable monomeric bis-allyl complex $CpTi(C_3H_5)_2$ in about 50% yield (Table 1). We also tried to prepare $CpTi(1\text{-}MeC_3H_4)_2$, starting from $CpTiCl_2$ by treatment with $1\text{-}MeC_3H_4MgCl$ at low temperature (-90°C) in THF. A red solution of the supposed bis-allylic complex was readily formed, but on warming to 0°C the solution turned brown while butenes were liberated. After extraction with pentane the well-known butadiene-methallyltitanium(II) complex $CpTi(\eta^4\text{-}C_4H_6)(\eta^3\text{-}1\text{-}Me\text{-}C_3H_4)$ was obtained in 30% yield [4]. The isolation of the thermally stable $CpTi(C_3H_5)_2$ makes the formation of the butadiene complex via disproportionation of $CpTi(1\text{-}MeC_3H_4)_2$ to $CpTi(1\text{-}MeC_3H_4)_3$ seem less probable.

Our interest in permethyl-substituted cyclopentadienyl ($Cp^\star$) derivatives led us to undertake the preparation of the possibly thermally more stable $Cp^\star Ti(C_3H_5)_2$. In order to prepare this compound we first prepared the hitherto unknown $Cp^\star TiCl_2(THF)$. This compound was prepared from $Cp^\star TiCl_3$ by zinc reduction and isolated analytically pure in about 30% yield. It contains exactly one weakly bonded THF ligand per Ti, in contrast to the Cp derivative, where an average of 1.5 THF per Ti was found [1b]. $Cp^\star Ti(C_3H_5)_2$ was isolated from the reaction of $Cp^\star TiCl_2(THF)$ with C_3H_5MgCl in low yield. Better yields were obtained when the $Cp^\star TiCl_2(THF)$ was not isolated, and it appears to be more convenient to use $Cp^\star TiCl_2(THF)$ prepared in situ from $TiCl_3(THF)_3$ and $Cp^\star Li$. From this reaction $Cp^\star Ti(C_3H_5)_2$ was isolated in 45% yield.

$CpVCl_2(PEt_3)_2$ has been used for the preparation of $CpV(C_3H_5)_2$ and of $CpV(1\text{-}MeC_3H_4)_2$ by treatment in ether with a stoichiometric amount of the appropriate allylic Grignard reagent. Unlike the earlier discussed benzyl derivatives, the phosphine ligands are completely liberated, and easily removed in vacuum. $CpV(C_3H_5)_2$ crystallizes nicely as dark needles from pentane solution, and was obtained in high yield (88%). The $1\text{-}MeC_3H_5$ derivative was obtained as a red oil. Crystallization of the complex is troublesome, possibly due to the presence of several

isomeric forms [8]. Unlike the titanium derivative, $CpV(1\text{-}MeC_3H_4)_2$ is, surprisingly, thermally stable towards butene elimination. No butene formation is observed in solutions of the compound at room temperature. $Cp'V(C_3H_5)_2$ was conveniently made from $Cp'VCl_2(PEt_3)_2$. All atttempts to prepare $Cp^\star V(C_3H_5)_2$ failed. The $Cp^\star V$ dihalide starting complex could not be prepared [2], and in situ reactions of supposed mono-$Cp^\star V$ species did not yield an identifiable bis-allyl compound.

An analogous reaction of $CpCrCl_2(THF)$ in THF with C_3H_5MgCl was carried out. At -80°C a red colour, possibly of $CpCr(C_3H_5)_2$, was observed, but upon warming to room temperature the solution turned dark. From this solution a dark product was isolated, the elemental analyses and molecular weight indicate the formation of $[CpCr(C_3H_5)]_2$. (Data are given in the Experimental Section.) The complex possibly contains bridging allyl ligands, as in $[(\eta^3\text{-}C_3H_5)Cr(\mu\text{-}C_3H_5)]_2$ [9].

Physical properties of the bis-allyl compounds

Data for elemental analyses, yields, DTA, etc., are summarized in Table 1. The elemental analyses are in agreement with the proposed stoichiometry. No reliable analyses could be obtained for the low melting compounds $Cp'V(C_3H_5)_2$ ($Cp' = \eta^5\text{-}C_5H_4Me$) and $CpV(1\text{-}MeC_3H_4)_2$. All the compounds are extremely air-sensitive, and very soluble in organic solvents such as pentane, ether or toluene and the solutions have a characteristic red colour. Molecular weight determinations (benzene) show the compounds to be monomeric (Table 1), and the light sensitivity of the titanium complexes is shown by a gradual increase in molecular weight when the benzene solutions are exposed to light. Poorly-soluble black oligomeric species are formed.

Thermal properties. DTA data (Table 1) show that the compounds are thermally stable at room temperature. The thermal stability of $Cp^\star Ti(C_3H_5)_2$ is markedly greater than that of $CpTi(C_3H_5)_2$, in accordance with the frequently observed increase in thermal stability when Cp is replaced by $Cp^\star$ [10]. The thermal decomposition of $CpM(C_3H_5)_2$ in toluene solution at 90°C was also studied. Formation of 0.49 equivalents of 1,5-hexadiene per metal atom for the Ti species and 0.47 equivalents of several hexadiene isomers per metal atom for the vanadium species was observed (GLC). Only traces of propene and no other C_3 compounds were

TABLE 1

ANALYTICAL AND PHYSICAL DATA FOR BIS-ALLYL COMPOUNDS

Compound	Yield (%)	Mol. weight (calcd.)	DTA		Allylic ν_a (CCC) (cm^{-1})	Analysis (found (calcd.) (%))			
			M.p. (°C)	Dec. temp. (°C)		Ti	V	C	H
$CpTi(C_3H_5)_2$	48	213 (195)	46	73	1495m	23.98 (24.55)	-	67.88 (67.71)	7.85 (7.75)
$Cp^\star Ti(C_3H_5)_2$	45	271 (265)	78	104	1485m	17.91 (18.06)	-	72.29 (72.44)	9.60 (9.50)
$CpV(C_3H_5)_2$	88	196 (198)	44	88	1510m	-	25.66 (25.70)	66.51 (66.67)	7.87 (7.63)
$Cp'V(C_3H_5)_2$	53	[a]	17	79	1512ms	-	[c]	[c]	[c]
$CpV(1\text{-}Me\text{-}C_3H_4)_2$	65	[a]	[b]	65	1538m	-	[c]	[c]	[c]

[a] Not determined. [b] Not observed. [c] No accurate data available due to the low melting point.

found in the products of these decompositions, and so only one allyl ligand per metal atom is eliminated. The obtained poorly soluble titanium and vanadium species are probably oligomeric, e.g. $[CpM(C_3H_5)]_n$. The molecular weight determination in benzene was rather inaccurate because of the low solubility, but it indicated that the vanadium species is possibly trimeric ($n = 3$). The solubility of the titanium species in benzene is even lower. Treatment of this latter species with HCl/ether gives $CpTiCl_3$ almost quantitatively, showing that the CpTi moiety is intact. The fate of the remaining allyl group was not established.

There is a striking analogy to the formation of $[CpCr(C_3H_5)]_2$. We presume that this compound is also formed by thermal decomposition of a bis-allyl complex, viz. $CpCr(C_3H_5)_2$.

IR. The IR spectra of $CpM(C_3H_5)_2$, $Cp^\star Ti(C_3H_5)_2$, $CpV(1\text{-}MeC_3H_4)_2$ and $Cp'V(C_3H_5)_2$ are all very similar and are readily interpreted. The characteristic Cp, Cp´ and $Cp^\star$ absorptions are at the expected positions. The absorptions of the allylic part deserve some more discussion. In all the spectra there is no allylic ν(C=C) band in the range 1580 to 1640 cm^{-1} and instead a ν_a(CCC) band is found in the range from 1485 to 1540 cm^{-1} (see Table 1), characteristic of η^3-coordination. We thus suggest that the allyl groups are both η^3-coordinated in our bis-allyl complexes. A small decrease of 10 cm^{-1} in ν_a(CCC) on replacement of Cp in $CpTi(C_3H_5)_2$ by $Cp^\star$ indicates a poorer π-acceptor ability of $Cp^\star$. The observed increase in ν_a(CCC) of 28 cm^{-1} in $CpV(1\text{-}MeC_4H_3)_2$ relative to $CpV(C_3H_5)_2$ is indicative for a *syn* position of the methyl ligand [11]; cf. 1509 cm^{-1} in $Cp_2Ti(\eta^3\text{-}C_3H_5)$ and 1533 cm^{-1} in $Cp_2Ti(\eta^3\text{-}syn\text{-}1\text{-}MeC_3H_4)$ [12].

NMR and ESR. The NMR and ESR spectra of the bis-allyl species clearly show the compounds to be paramagnetic, as expected for 15 electron titanium(III) compounds with one unpaired electron and 16 electron vanadium(III) compounds with two unpaired electrons. The ^1H NMR spectra were recorded at 20°C from 500 ppm downfield to 500 ppm upfield from TMS. In this range no resonances were observed for $CpTi(C_3H_5)_2$ and for $Cp^\star Ti(C_3H_5)_2$ only one broad resonance at 7 ppm low field from TMS, probably due to $Cp^\star$ protons. The ^1H NMR spectrum of $CpV(C_3H_5)_2$ showed an extremely broad ($\Delta\nu_{1/2} \sim 10.000$ Hz) resonance around 180 ppm downfield from TMS, probably due to both allyl and Cp protons. For $Cp'V(C_3H_5)_2$ two additional broad resonances were found at 35 and 31 ppm (area ratio ~ 1/2 respectively) downfield from TMS, which we attribute to the methyl group in Cp´. Their positions fall in the range found for Me in Cp´ of other trivalent vanadium complexes [13]. The presence of two closely spaced resonances might indicate the presence of two conformational isomers, of which an *endo-exo* isomer is possibly the dominant species for steric reasons.

The ESR spectra of $CpTi(C_3H_5)_2$ and $Cp^\star Ti(C_3H_5)_2$ in THF and pentane show a singlet at $g = 2.002$ and $g = 2.000$ respectively, as expected for these monomeric titanium(III) compounds. THF does not seem to affect the spectra of the bis-allyl complexes. The ESR studies also confirmed the light sensitivity; a pentane solution of $CpTi(C_3H_5)_2$ gives a black precipitate formed upon exposure to light. The products are presumably diamagnetic as the singlet disappears and no new resonances appear. In THF a different behaviour is found. Two new singlets are formed at $g = 2.012$ and $g = 1.993$. The results indicate that in pentane disproportionation can ultimately occur to titanium(II) and titanium(IV) species, while in THF this disproportionation is prevented. For $CpV(C_3H_5)_2$ no ESR signal was observed.

Chemical properties of bis-allyl compounds

The chemical reactivity of $CpM(C_3H_5)_2$ towards a variety of substrate molecules, like carbon monoxide, acetylenes, alkenes and hydrogen, was briefly examined. In most cases the identification of the organometallic products was troublesome due to formation of complicated mixtures, and the very limited information that NMR techniques give in these paramagnetic systems.

With acetylenes. $CpV(C_3H_5)_2$ shows no activity towards acetylenes such as tolane or 2-butyne under ambient conditions. $CpV(C_3H_5)_2$ was isolated almost quantitatively after one day. In contrast $CpTi(C_3H_5)_2$ reacts rapidly with these acetylenes, but the nature of the products is not yet clear.

With CO. $CpV(C_3H_5)_2$ reacts smoothly with CO at ambient conditions. ($t_{1/2}$ 90 min, 24°C), with quantitative formation of $CpV(CO)_4$ and 1,5-hexadiene. Reductive coupling of allyls to dienes is more often observed in CO reactions. For instance $Ni(C_3H_5)_2$ reacts with CO quantitatively to $Ni(CO)_4$ and 1,5-hexadiene [14]. The reaction of $CpTi(C_3H_5)_2$ with CO is of special interest in comparison with the related titanium(III) compound $Cp_2Ti(\eta^3\text{-}C_3H_5)$, where triallylmethanol is formed directly in an aprotic medium [15]. A very fast reaction of $CpTi(C_3H_5)_2$ with CO (1 bar) is observed, in which about 1.5 equivalents of CO are consumed per titanium atom ($t_{1/2}$ 1.5 min, 24°C). Unfortunately identification of the products was not possible. The absence of a ν(CO) band at 1500-2100 cm^{-1} in the IR spectrum of the obtained pyrophoric black powder indicates the absence of a CO ligand in this product, and reduction of the CO bond well below C=O. No alcohol or ketone could be identified by GLC. Elimination of some propene and 1,5-hexadiene was established. $CpTiCl_3$ is formed almost quantitatively when the residue is treated with HCl/ether, but no satisfactory information on the fate of carbon monoxide was obtained.

Isomerization of alkenes. No reaction of $CpTi(C_3H_5)_2$ or $Cp^{\star}Ti(C_3H_5)_2$ with alkenes is observed (under N_2) even in refluxing 1-hexene. These complexes are not active in the catalytic isomerization of alkenes. In contrast $CpV(C_3H_5)_2$ readily isomerizes alkenes. As examples we will discuss the isomerization of 1-pentene and 1-hexene, for which the alkenes were also used as solvent. In Fig. 1 the isomerization of 1-pentene under reflux (30-35°C) is represented, and Fig. 2 shows the isomerization of 1-hexene at 35°C.

In the first stage of the reaction *trans*-alkenes are formed almost exclusively in a kinetically controlled process. The initial *cis-trans* ratio of formed 2-alkenes is about 1/37 for pentene and 1/57 for hexene. A maximum is found for *trans*-2-pentene after 1.5 h (95% present), for *trans*-2-hexene after 1 h (80% present) and for *trans-3*-hexene after 3 h (23% present). Subsequently, slow *cis-trans* isomerizations occur, with substantial formation of *cis*-2-alkenes, and in which only a minor trace of *cis*-3-hexene is formed (< 0.5%, not shown in Fig. 2). In both systems the final alkene ratio approaches the thermodynamic equilibrium value [16,17]. The isomerization of 1-hexene under reflux (63-68°C) follows an almost identical course; the maximum for *trans*-2-hexene is already observed after 2.5 min (78% present), and the initial conversion rate of 1-hexene to *trans*-2-hexene exceeds 6000 equivalents per vanadium per h.

During the isomerization propene is formed, but no hexadienes or larger dienes were observed. We thus assume that no substantial thermal decomposition of CpV-bis-allyl takes place during the isomerization. Treatment of the organometallic

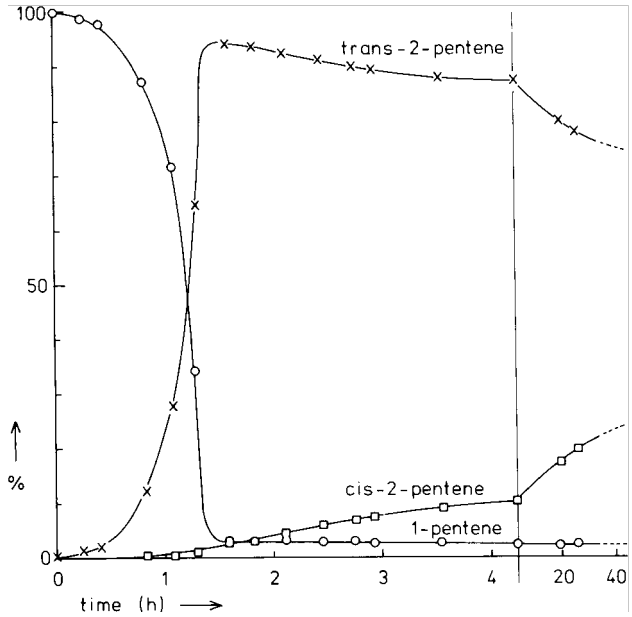


Fig. 1. Isomerization of 1-pentene with $CpV(C_3H_5)_2$ under reflux (30-35°C); molar ratio 1-pentene/V = 125.

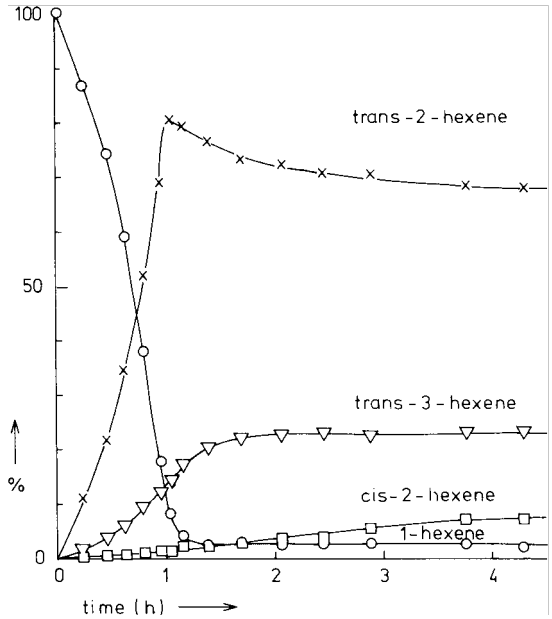
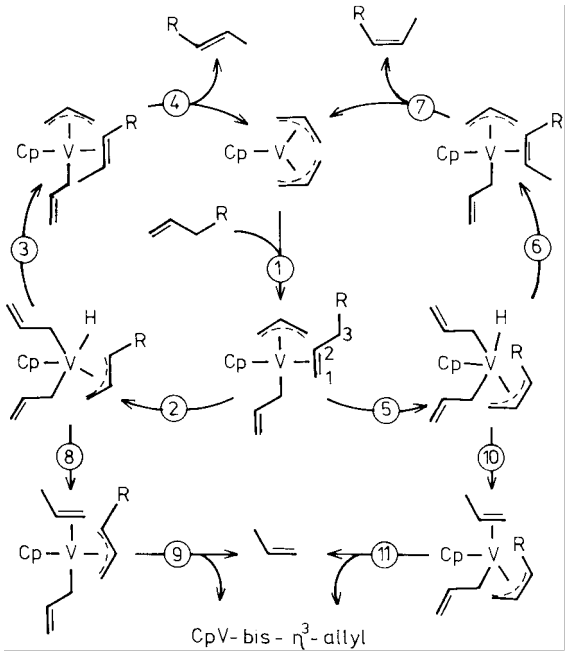


Fig. 2. Isomerization of 1-hexene with $CpV(C_3H_5)_2$ at 35°C; molar ratio 1-hexene/V = 199.

residue with CO (1 bar, 25°C) gives $CpV(CO)_4$ and some $Cp_2V_2(CO)_8$ but no 1,5-hexadiene, octadiene or nonadiene, indicating that all of the original C_3H_5 ligands are finally replaced and that the CpV moiety keeps intact.

Addition of oxygen to the mixture immediately inhibits the isomerization; it effectively blocks the coordination sites for alkene addition. Addition of one PEt_3 per vanadium atom also stops the isomerization; this shows that PEt_3 can coordinate to CpV-bis-allyl and that it binds more strongly than alkenes.

Isomerization with addition-elimination of a metal hydride to the alkene, i.e. via alkylmetal species, affords the initial presence of a metal hydride complex. $CpV(C_3H_5)_2$ lacks hydride ligands and the only hydride source is the alkene reagent/solvent. Spontaneous intramolecular reactions with formation of vanadium hydrides are unlikely, and the isomerization takes place without the need for activation by H_2. Thus the most likely mechanism for the isomerization of alkenes with $CpV(C_3H_5)_2$ is a π-allylmetal hydride process [18]. The formation of an π-allylmetal hydride species from an alkene adduct corresponds to oxidative addition. $CpV(C_3H_5)_2$ with its central trivalent vanadium ion with two unpaired electrons looks especially suitable for this type of addition reaction; the formal oxidation state of vanadium is raised by two from three to five. Moreover, the inactivity of titanium derivatives suggests an intermediate species which is not attainable for titanium, e.g. a pentavalent species. The proposed reaction sequence, resulting in an overall 1,3-hydrogen shift, is shown in Scheme 1. The first step (1) is thought to be the coordination of alkene. An $\eta^1 \rightarrow \eta^3$ rearrangement of one of the π-allyl ligands then creates a site for alkene coordination. The next step is hydrogen abstraction from the sp^3 carbon atom adjacent to the double bond, with formation



SCHEME 1. Proposed reaction sequence for the isomerization of alkenes with $CpV(C_3H_5)_2$.

of pentavalent π-allylmetal hydride species. There are two possible conformational forms, having R in a *syn* or an *anti* position (steps 2 and 5). The *syn* position for R is sterically favoured and more stable, as is generally observed in transition metal complexes [19]. This explains the initial preferential formation of *trans*-alkenes, because re-addition of the hydride- to carbon-1 instead of carbon-3 gives a *trans*-alkene complex from the favoured *syn* isomer (step 3) and a *cis*-alkene complex from the *anti*-isomer (step 6). The final steps 4 and 7 in the two cycles are the elimination of isomerized alkenes. The sequence also accounts for the formation of propene by re-addition of the hydride to a C_3H_5 ligand. In this way the original allyl ligands are gradually replaced by substituted allyls. The CpV-bis-allyl structure remains intact, which is also consistent with the unchanged brown-red colour of the reaction mixture.

The initial conversion rate of 1- to 2-alkenes is clearly reflected in the observed evolution rates of propene. This suggests that CpV-bis-allyl complexes with substituted allyl ligands are more effective in isomerization, and it is clear, of course, that the proposed $\eta^3 \rightarrow \eta^1$ rearrangement of a π-allyl ligand in alkene coordination is easier for a pentenyl and even more so for a hexenyl ligand, than for a propenyl ligand.

With H_2: $CpM(C_3H_5)_2$ (M = Ti,V) and $Cp^{\star}Ti(C_3H_5)_2$ react with H_2 at ambient conditions with elimination of one C_3H_5 ligand as propane. The poorly soluble dark organometallic products have not been identified. With $CpTi(C_3H_5)_2$ or $Cp^{\star}Ti(C_3H_5)_2$ no isomerization of alkenes occurs even when H_2 is added; surprisingly, the isomerization reactions with $CpV(C_3H_5)_2$ slow down when H_2 is added. Some slow hydrogenation of α-alkenes is observed, but when the α-alkenes are isomerized to internal alkenes, hydrogenation virtually stops. Moreover, when $CpV(C_3H_5)_2$ is first treated with H_2 at room temperature in pentane solution for one day, no activity in isomerization nor hydrogenation is found. With the titanium compounds, however, hydrogenation readily occurs, in competition with substantial oligomerization. For instance ethylene is oligomerized up to C_{16}. The specificity in the formation of branched α-alkenes favours a reaction pathway involving a titanacyclopentane intermediate [20]. These reactions are presently under investigation.

Experimental

General remarks

All experiments were carried out under nitrogen by Schlenk or glovebox techniques. Solvents were distilled from sodium-potassium melts or sodium under nitrogen. $CpTiCl_2$ [1d], $Cp^{\star}TiCl_3$ [10], $CpVCl_2(PR_3)_2$ [2] and $CpCrCl_2(THF)$ [21] were prepared by published procedures. CO and H_2 were used without purification.

Elemental analyses were performed at the Microanalytical Department of the Chemical Laboratories of Groningen University. Molecular weights were determined by cryoscopy in benzene. Melting points and decomposition temperatures were determined by differential thermal analysis (DTA), with a heating rate of 2-3°C/min.

IR spectra were measured on a Jasco-IRA-2 spectrophotometer as Nujol mulls between KBr discs or neat between KBr discs for liquid samples. 200 MHz ^{1}H NMR spectra were recorded by Drs R.J. Bouma on a Nicolet NT 200 spectrometer equipped with a Nicolet model 1180 data system. ESR spectra were recorded at -30°C on a Varian E-4 ESR spectrometer with DPPH as external reference.

GLC analyses on liquid samples were performed on a Packard Becker 428 GC instrument equipped with a 25 m × 0.25 m × 0.24 mm (i.d.) glass capillary column, wall coated with SE 30. Gaseous samples were analyzed with a Hewlett Packard 5750-G and a 7620-A Research Chromatograph using a Porapack Q (2 m × 1/8") and a Porasil B (2 m × 1/8") column. Reactions with gases were performed using an automatic gas-buret and a Töpler pump.

Preparation of $CpTi(CH_2Ph)_2$

A solution of 18.0 mmol of $PhCH_2MgBr$ in ether was added dropwise in 1.5 h to a stirred suspension of 1.66 g (9.00 mmol) of $CpTiCl_2$ in 100 ml of ether at 0°C. A yellow-brown solution was formed, and this was stirred at 0°C for 4 h. The solvent was removed in vacuo and the product extracted with 150 ml of pentane. Crystallization by slow cooling to -80°C gave 0.57 g (22%) of brown $CpTi(CH_2Ph)_2$. Elemental analyses: found (calcd.) (%): Ti, 16.52 (16.22); C, 77.33 (77,29); H, 6.60 (6.49). Dec. temp. 91°C. No ^1H NMR resonances were observed.

Preparation of $CpV(CH_2Ph)_2$ and $CpV(CH_2Ph)_2(PMe_3)$

A solution of 12.30 mmol of $PhCH_2MgBr$ in ether was added dropwise in 1 h to a solution of 2.61 g (6.16 mmol) of $CpVCl_2(PEt_3)_2$ in 100 ml of ether at -80°C. A dark red solution was formed. This was warmed to room temperature and stirred for 1 h. The solvent was removed in vacuo and to remove PEt_3 the resulting dark oil was stirred twice with 50 ml of pentane and the solvent evaporated off in each case. Finally the red oil obtained was extracted with 200 ml of pentane, and the extract was concentrated to 40 ml and slowly cooled to -80°C. Dark crystals separated, but removal of the solvent and warming to 0°C again gave a red oil, the IR spectrum of which still showed the presence of a small amount of coordinated PEt_3. Several washings with small portions of pentane at 0°C did not remove all the phosphine. No elemental analyses were performed. An HCl/ether reaction gave 1.857 equivalents of toluene per vanadium atom (GLC) using *o*-xylene as internal reference. This result is consistent with formation of $CpV(CH_2Ph)_2$.

A reaction starting from $CpVCl_2(PMe_3)_2$ was carried out in exactly the same way as described above for $CpVCl_2(PEt_3)_2$. A dark solid was obtained in 81% yield (based on V). Recrystallization was from pentane and ether, and the elemental analysis approached that of $CpV(CH_2Ph)_2(PMe_3)$. Analysis: found (calcd.) (%): V, 12.52 (13.61); C, 69.60 (70.58); H, 7.57 (7.54).

Preparation of $CpTi(C_3H_5)_2$

A solution of 24.7 mmol of C_3H_5MgBr in ether was added dropwise during 1.5 h to a stirred suspension of $CpTiCl_2$ (2.28 g, 12.4 mmol) in 150 ml of ether at 0°C. A dark red solution was formed, and this was stirred at 0°C for 1 h then the solvent was removed in vacuo. The resulting solid was extracted with 300 ml of pentane. Crystallization by slow cooling from a concentrated pentane solution gave $CpTi(C_3H_5)_2$ as a dark micro-crystalline powder in 48% yield. Elemental analyses and DTA data are given in Table 1. The reaction mixture was carefully protected from light to prevent the slow formation of a poorly soluble, black product.

Preparation of $Cp^\star TiCl_2(THF)$

A solution of 2.48 g (8.57 mmol) of $Cp^\star TiCl_3$ in 50 ml of THF was stirred for 16

h with 1.14 g (17.4 mmol) of zinc powder at room temperature. The red colour changed rapidly to green, and thereafter a blue solution formed gradually. After filtration, the extract was concentrated to 20 ml and slowly cooled to -30°C. Clear blue crystals of $Cp^{\star}TiCl_2(THF)$ separated. After decantation of the solvent, the crystals were dried in vacuo at 0°C. In order to remove all the $ZnCl_2$, the complex was recrystallized from THF. Yield 29%. Elemental analysis: found (calcd.) (%): Ti, 14.74 (14.69); Cl, 21.74 (21.74); C, 51.49 (51.56); H, 7.04 (7.11).

The THF is only weakly coordinated. In vacuum at room temperature THF is lost at appreciable rate, and a green product is formed. After several washings with pentane this product analyzed as $Cp^{\star}TiCl_2$. Upon re-addition of THF blue $Cp^{\star}TiCl_2(THF)$ is obtained again, but not in quantitative yield; a small amount of $Cp^{\star}TiCl_3$ is formed by disproportionation and this makes the THF-free complex less suitable as starting compound for preparations.

Preparation of $Cp^{\star}Ti(C_3H_5)_2$

A solution of 3.53 g (9.53 mmol) of $TiCl_3(THF)_3$ in 100 ml of THF was stirred with 1.40 g (9.86 mmol) of $Cp^{\star}Li$ at room temperature for 2 days. The resulting blue solution of $Cp^{\star}TiCl_2(THF)$ was cooled to -80°C and a solution of 19.2 mmol of C_3H_5MgCl in THF was added dropwise during 1 h. The red solution obtained was warmed to 0°C and stirred for 2 h. The solvent was removed in vacuo and the resulting dark solid extracted with 300 ml of pentane. Concentration to 50 ml and slow cooling to -80°C yielded 1.14 g (45%) of brown-red crystals of $Cp^{\star}Ti(C_3H_5)_2$. Elemental analysis and DTA data are given in Table 1. During this preparation the product was protected from light to avoid decomposition.

Preparation of $CpV(C_3H_5)_2$

A solution of 26.5 mmol of C_3H_5MgBr in ether was added dropwise during 1 h to a solution of 5.5 g (13.2 mmol) of $CpVCl_2(PEt_3)_2$ in 150 ml of ether kept at -80°C. A dark red solution formed. After warming to room temperature and stirring for another hour, the solvent was removed in vacuo. The resulting dark solid was extracted with 300 ml of pentane. Concentration of the pentane solution to 50 ml and subsequent slow cooling to -80°C gave dark crystals of $CpV(C_3H_5)_2$, yield 88%. For elemental analysis and DTA data see Table 1. The mass spectrum showed a parent peak at *m/e* 198.

Preparation of $Cp'V(C_3H_5)_2$ and $CpV(1\text{-}Me\text{-}C_3H_4)_2$

$Cp'V(C_3H_5)_2$ and $CpV(1\text{-}Me\text{-}C_3H_4)_2$ were prepared by the procedure used for $CpV(C_3H_5)_2$. $Cp'V(C_3H_5)_2$ was isolated at low temperature (< 0°C) to avoid melting of the crystals. $CpV(1\text{-}MeC_3H_4)_2$ was found difficult to crystallize; crystals were obtained by very slow cooling to -80°C, but due to the very low melting point the compound could only be isolated as a red oil. IR spectra showed both compounds to be free of phosphine. No reliable elemental analyses were obtained.

Thermal decomposition of $CpM(C_3H_5)_2$

Thermal decomposition reactions of $CpM(C_3H_5)_2$ (M = Ti, V) were performed on a 1 mmol scale in toluene (15 ml) solution under vacuum in a closed vessel, with benzene as internal reference. The solutions were stirred for 2 h at 90°C, cooled in liq. N_2 to trap all products, and analyzed by GLC.

Preparation of [CpCr(C_3H_5)]$_2$

A solution of 15.9 mmol of C_3H_5MgCl in 30 ml of THF was added dropwise during 1.5 h to a blue solution of 2.08 g (8.01 mmol) of $CpCrCl_2$ (THF) in 100 ml of THF at -80°C. A brown-red solution was formed. After warming to room temperature and stirring for 16 h, the solvent was removed in vacuo and the resulting dark solid extracted with 150 ml of pentane. Slow cooling to -80°C gave 0.36 g (28%) of dark $[CpCr(C_3H_5)]_2$. Elemental analysis: found (calcd.) (%): Cr, 32.81 (32.88); C, 60.43 (60.75); H, 6.42 (6.37). Molecular weight found (calcd.) in benzene: 319 (316). M.p. 79°C and dec. temp. 86°C.

Isomerization of alkenes with $CpV(C_3H_5)_2$

Alkenes were passed through Al_2O_3 before use. $CpV(C_3H_5)_2$ (~ 1 mmol) was dissolved in the alkene (~ 150-200 mmol) and the isomerization was followed by GLC. For reactions under reflux, small samples were taken from the vapour close to the liquid surface by means of a cooled syringe. For 1-hexene isomerization at 35°C, the samples were taken from the liquid, filtered after air oxidation, and analyzed. Complete inhibition of the isomerization reaction on addition of air was noticed, and so these samples give a good indication of the actual hexene ratios in the reaction mixture at the moment of removal. For convenience, the peak area ratios of the alkenes in the chromatograms were assumed to correspond to molar ratios. In this way Fig. 1 and 2 were obtained.

The remaining solutions were stirred under CO (1 bar, 25°C) for one day and transferred to a Florisil column. Chromatography yielded $CpV(CO)_4$ and some $Cp_2V_2(CO)_5$, identified by their ^1H NMR spectra in benzene-d_6 [22]. The solution was analyzed by GLC.

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